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A group contribution method for estimating the vapour pressures of α-pinene oxidation products

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Abstract

A prediction method based on group contribution principles is proposed for estimating the vapour pressure of α-pinene oxidation products. Temperature dependent contributions are provided for the following chemical groups: carbonyl, nitrate, hydroxy, hydroperoxide, acyl peroxy nitrate and acid. On the basis of observed vapour pressure differences between isomers of diols and dinitrates, a simple refinement is introduced in the method, which allows to account for the influence of the substitutions on the vapour pressure for the hydroxy and nitrate functionalities. In general, the predicted vapour pressures of multifunctional compounds show a better agreement with experimental data (within a factor 2–3) than the UNIFAC method (Asher et al., 2002). Among the α-pinene products identified to date, pinic acid and hydroxy pinonic acid are predicted to be the least volatile compounds, with estimated vapour pressures of 3×10^{-6} torr and 6×10^{-7} torr, respectively. The vapour pressure of the other primary products range from 10^{-5} to 10^{-3} torr, with hydroxy hydroperoxides presenting the lowest values. Noting that multifunctional carboxylic acids, in particular pinic acid, are believed to be mostly present as dimers in laboratory conditions, we suggest that the partial vapour pressure of the pinic acid dimer should be close to the experimental subcooled vapour pressure for pinic acid (estimated at $\sim10^{-6}$ torr) due to its large contribution to the total concentration (dimer+monomer) in experimental conditions.

1. Introduction

Monoterpenes are important constituents of biogenic VOC emissions. Among the monoterpenes, α-pinene is observed to have the highest emission rates and to be the most abundant (Guenther et al., 1995). The vapour pressures of its oxidation products range from 10^{-2} torr to 10^{-7} torr (Hallquist et al., 1997; Hoffmann et al., 1997; Bilde and Pandis, 2001). The least volatile of these products can enter the aerosol phase and form secondary organic aerosol (SOA) (Kanakidou et al., 2005). The partitioning of a

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compound i between the gas and aerosol phases has been parameterized by Pankow (1994a,b):

$$K_{p,i} = \frac{760RTf_{om}}{MW_{om}10^6\zeta_i p^0_{L,i}}, \quad (1)$$

where R is the ideal gas constant; T is temperature; MW_{om} is the mean molecular weight of the absorbing medium; f_{om} is the weight fraction of the total suspended particulate material that constitutes the absorbing om phase; ζ_i is the activity coefficient of compound i in the particulate phase, generally assumed to be close to unity (Kamens et al., 1999) and $p^0_{L,i}$ is the subcooled vapour pressure of compound i at temperature T.

The vapour pressure of a compound measures its ability to escape from the condensed phase, which depends on the strength of the intermolecular forces existing between the condensed molecules. The relatively weak dispersion forces (resulting from temporary dipoles formed in adjacent molecules) are the sole cohesive agent in liquid alkanoic compounds, which explains their high vapour pressures. In oxygenated compounds, cohesion is reinforced by the hydrogen bonds existing between the polar groups of the molecules (Poling et al., 2001). Due to the important role played by these hydrogen bonds, the vapour pressure of an oxygenated organic compound is strongly dependent on the number and type of oxygenated functionalities, as well as on the carbon structure (e.g. carbon number, nature and positions of the branchings) of the molecule.

The products of the oxidation of α-pinene by OH (Peeters et al., 2001; Capouet et al., 2004) and O_3 (Saunders et al., 2003) bear one or several oxygenated groups among the carbonyl, hydroxy, nitrate, hydroperoxide and acid functionalities. Experimental data are lacking for the thermodynamic properties of a large majority of these products. In this paper, we describe a semi empirical extrapolation method for predicting the vapour pressure of the α-pinene oxidation products. Given their large number, this method is meant to be relatively simple and straightforward to apply. It is based on the

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so-called “group contribution” principles.

2. Group contribution principles

Group contribution methods attempt to correlate structural molecular properties (descriptors) with mathematical functions representing a chemical property of a molecule for a category of compounds by means of statistical methods. The descriptors are usually atom groups. Their “contributions” are obtained by fitting an adopted mathematical function to a set of experimental data. These estimation methods are therefore essentially empirical. A group contribution method expresses the thermodynamic property of a chemical compound such as its vapour pressure as a function of a sum of contributions $\tau_i(T)$ of small groups of atoms i constituting the molecule:

$$p = f\left(\sum_i \tau_i(T)\right). \quad (2)$$

A large variety of group contribution methods have been designed in the past years, differing in their field of applicability and in the set of experimental data they are based on.

Jensen et al. (1981), Joback and Reid (1987), Chein-Hsiun (1994) and Li et al. (1994) proposed such methods for the prediction of a variety of thermodynamic properties (e.g. vapour pressure, critical temperature, critical pressure, boiling point) of organic compounds. These predictive methods are based on different data sets and provide estimations for specific or various classes of compounds including alkanes, alkenes, aromatics, halogenated hydrocarbons, oxygen-, sulfur- or nitrogen-containing monofunctional compounds. Other approaches have been proposed to estimate the vapour pressure of a component: e.g. Makar (2001) adopted an approach where the vapour pressures are directly estimated from polynomials, functions of the carbon number and temperature, defined for 39 structural classes. Myrdal and Yalkowsky (1997) proposed

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a method which requires the knowledge of the normal boiling point as well as structural information related to the molecule flexibility.

In recent years, the experimental identification of multifunctional compounds in secondary organic aerosols has strengthened the need for new prediction methods dedicated to these complex species. Marrero and Gani (2001) and Olsen and Nielsen (2001) developed methods which perform estimations at different levels. While the primary level describes a wide variety of simple, monofunctional groups, the higher levels treat multifunctional structures and allow to differentiate between isomers by considering, to some extent, the interactions among functionalities. Asher et al. (2002) developed a method based on the principles of UNIFAC (Universal Functional Group Activity Coefficients, Fredenslund et al., 1977). It provides vapour pressure estimates of mono- and multifunctional oxygen-containing species using only 12 group contributions.

Vapor pressure estimates of monofunctional species by current methods are reasonably accurate. An evaluation of several methods performed by Asher et al. (2002) shows that the vapour pressures of volatile compounds having $\log_{10} p^0_{L,i} \geq -3$ at ambient temperature are predicted by current methods to within a factor 2 on average. For less volatile compounds (often multifunctional), i.e. $\log_{10} p^0_{L,i} \leq -5$, uncertainties are estimated to a factor 3 for the UNIFAC method and up to an order of magnitude for other methods. This explains the broad use of UNIFAC in SOA models (Griffin et al., 2005). The failure to provide more accurate predictions for low volatile compounds is related in part to experimental difficulties. Measurements of low vapour pressures are easily contaminated by impurities or biased by adsorption of the organic on the reactor walls. The literature reports experimental vapour pressure measurements for only about one hundred multifunctional compounds. The relative uncertainty of their measurements, when known, ranges from 25% to 50% (Hallquist et al., 1997; Bilde and Pandis, 2001; Bilde et al., 2003). Another important cause for the inaccuracy in the predictions for multifunctional compounds is the poorly quantified role of interactions between the chemical functionalities. Although they appear to have a large impact on the vapour pressure, their quantification remains difficult in part because of the scarcity of data for

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these compounds.

A major drawback of the methods described above is the absence of parameterization for chemical classes believed to play an important role in SOA formation (e.g. organic nitrates). The vapour pressure estimation method described in this work is intended to provide vapour pressure predictions for broad categories of α-pinene degradation products including alcohols, acids and carbonyls (classes which were considered by the methods cited above) as well as nitrates, peroxy acyl nitrates (PANs) and hydroperoxides (which were ignored by these methods).

3. Method proposed in this work

The literature sources for the vapour pressure data used in this study are listed in Table 1 (last column). The vapour pressures at 298 K for a selection of compounds are shown as a function of carbon number in Fig. 1. As seen on this figure, it is important to distinguish between linear (single-chained) compounds, denoted by the prefix "n-" or "1,n", and the other compounds, including, cyclic, alkyl substituted species and/or species with a functionality not positioned at one extremity of the molecule. The "tri-O-acids"(Table 1) class follows the definition chosen by Makar (2001). This class represents three-oxygen-acids, i.e., acids with a carbonyl or hydroxy functionality.

Note that all species listed in Table 1 are either mono- or difunctional. Based on the group contribution principles, and in absence of data for species bearing more than two functionalities, we assume the method to be applicable to all multifunctional species. Figure 1 shows that there is a roughly linear relationship between the logarithm of the vapour pressure and the carbon number, with an approximately constant slope for all classes, especially for n≥4. A noticeable exception to this pattern is provided by the diacids. Bilde et al. (2003) has shown that the vapour pressures of solid C_3-C_9 dicarboxylic acids depend strongly on the parity of the carbon number. This is due to the increased symmetry of even-numbered molecules, favoring the stability of their crystal structure. Rosenorn et al. (2003) reported that methyl substituted even-

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numbered diacids have significantly higher vapour pressures than their non-substituted analogues, presumably because of their asymmetry. The vapour pressure of these compounds show no dependence on parity. Note that the *1,n*-diacids and $C_{\geq 7}$ *1,n*-diols are solid at ambient temperature, whereas the other compounds reported in Fig. 1 are liquid. The (subcooled) liquid vapour pressures of solid compounds shown in this figure are obtained by converting p_s^0 into p_L^0 using the equation described in Prausnitz (1969):

$$\ln p_s^0(T) = \ln p_L^0(T) - \left(\frac{\Delta S_{\text{fus}}(T_m)}{R} \left(\frac{T_m}{T} - 1 \right) \right). \quad (3)$$

The melting point T_m and the fusion entropy change $\Delta S_{\text{fus}}(T_m)$ are provided by NIST (2004) for *1,n*-diacids and $C_{\geq 7}$ *1,n*-diols. Figure 1 also shows that the vapour pressures of different isomers of dinitrates and diols sometimes cover several orders of magnitude, with the *1,n*-compounds presenting the lowest values. Our prediction method aims at reproducing to some extent the differences in vapour pressure between different isomers.

The proposed method to estimate the vapour pressure of a compound *i* at temperature *T* has the following form:

$$\log_{10} p_{L,i}^0(T) = \log_{10} p_{L,hc}^0(T) + \sum_k^n \nu_{k,i} \tau_k(T). \quad (4)$$

Here $p_{L,hc}^0(T)$ is the vapour pressure of the "parent" alkanoic compound *hc*, where all oxygenated functionalities in compound *i* are replaced by hydrogen atoms (e.g. -CH(OH)- is replaced by $-CH_2-$, etc.), $\nu_{k,i}$ is the number of oxygenated functionalities of type *k* in the compound *i*, *n* is the number of defined types of oxygenated functionalities, and τ_k are the group contribution parameters. When no experimental value of the vapour pressure for the parent compound is available, the group contribution method of Marrero and Gani (2001) is used to calculate the boiling point, the critical temperature and the critical pressure of the compound i. $p_{L,i}^0(T)$ is obtained using the Lee and Kesler formulation, function of these properties (Poling et al., 2001). The choice

of the method of Marrero and Gani (2001) is motivated by its good performance for alkanoic compounds. A comparison study by these authors shows that their method performs better than the Joback and Reid (1987) method which is commonly used for the prediction of these thermodynamic parameters. We estimate that the error on $p^0_{L,hc}$ predicted using Marrero and Gani (2001) does not exceed 50%, even in the case of the most complex structures of VOC.

Table 2 lists the temperature dependent contributions optimized in this work. Note that the group contributions for the nitrate and hydroxy functionalities depend on the degree of substitution of the carbon bearing the functionality. The importance of this distinction can be illustrated by the observed lower vapour pressures of 1,6-hexanediol and butane-diol-1,2, compared to their substituted isomers 2,3-dimethyl-2,3-butanediol and 2-methyl propane-diol-1,2 (Fig. 1). Only a minor part of this difference is related to the weaker dispersion forces existing in substituted hydrocarbons, as shown by the small difference (30%) observed between the vapour pressures of the corresponding alkane isomers. The rest can be attributed to the interactions produced by the hydroxy functionalities. Their strength depends on the location of the chemical functionalities and the distance between each other in the molecules. This relatively minor influence of the dispersion forces explains the smaller error expected in the prediction of $p^0_{L,hc}(T)$ compared to the second term of Eq. (4) representing the influence of the functionalities. The effect of distance between functionalities has been investigated by Knauth and Sabbah (1990a,b,c). They have shown that, when the hydroxy functionalities are positioned close to each other in linear diols, intramolecular hydrogen bonds between the hydroxy functionalities are favored, resulting in less intermolecular cohesion and therefore in higher vapour pressures. Parameterizing both effects (presence of substitutions and distance between functionalities) simultaneously would require more data than is currently available. Our choice to take into account the effect of alkyl substitutions on the α carbon of the functionalities is motivated by the large number of substitutions in the α-pinene oxidation products. Furthermore, this approach allows to include also some influence of the distance between the functionalities, since this

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distance is usually larger in primary diols and dinitrates from the data set than in their secondary isomers. An exception to this rule is provided by the case of the *para*-diols and *para*-dinitrates cyclic compounds. As for the linear diols, the effect of intramolecular interactions between two hydroxy groups can be seen in the vapour pressure data for cyclic diols and dinitrates. For example, the vapour pressure of cyclohexanediol isomers is seen to increase when the distance between the hydroxy groups decreases. 1,4-cyclohexanediol and 1,6-hexanediol are found to have similar vapour pressures, reflecting the fact that the hydroxy groups are situated at the respective opposites of the carbon structure in both molecules. Therefore, although the hydroxy groups of 1,4-cyclohexanediol are, strictly speaking, secondary, they are considered as primary in our parameterization of group contributions. Note that, in absence of vapour pressure data for tertiary and secondary (di)nitrates at different temperatures, the temperature dependence of their contributions is derived from the primary dinitrate contribution.

Since linear monoaldehydes and monoketones of same carbon number show very close vapour pressures, both functionalities are treated using a single contribution parameter τ_{carb}. The linear diacids of even carbon number are not taken into account in the determination of the acid contribution, since their symmetric structure (resulting in abnormally low vapour pressures) is not characteristic of the α-pinene oxidation products. Vapor pressure data are scant for the hydroperoxides and peroxy acyl nitrates (PANs). The contributions shown in Table 2 for these classes are based on data for only three monofunctional hydroperoxides and one peroxy acyl nitrate (peroxy acetyl nitrate).

The principles of our prediction method are illustrated by the two following examples. In both cases, the Marrero and Gani (2001) method combined with the Lee and Kesler equation is used to predict the vapour pressure of the parent alkanoic compound, whose the structure is shown in Fig. 2. Consider first, APINANO3, a hydroxy nitrate produced from the oxidation of α-pinene by OH (Saunders et al., 2003). Given the presence of a tertiary nitrate and a secondary hydroxy functionality in APINANO3, its vapour pressure at 298 K is estimated as:

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$\log_{10} p^0_{L,hc}$	=0.4232
$-1\times\tau_{ONO2t}$	−1.2793
$-1\times\tau_{OHs}$	−2.0374
$\log_{10} p^0_{L,APINANO3}$	=−2.89351

The second example is provided by pinic acid, a low volatility product formed in the ozonolysis of α-pinene (Saunders et al., 2003). The vapour pressure of pinic acid at 320 K is estimated as:

$\log_{10} p^0_{L,hc}$	=1.6135
$-2\times\tau_{COOH}$	−6.1732
$\log_{10} p^0_{L,pinic\ acid}$	=−4.5597

4. Minimization and comparison with the UNIFAC method

The parameters τ_k are determined by the minimization of a cost function J defined as

$$J = \frac{1}{2}\sum_i^N \frac{\left(\log_{10}\ p^{0,mod}_{L,i} - \log_{10}\ p^{0,exp}_{L,i}\right)^2}{(E_i)^2}. \quad (5)$$

The cost function J measures the bias between the model and the entire set of available data (N species) listed in Table 1. Being a quadratic function of τ_k, its minimization is straightforward. The minimization has been performed at two temperatures (298 K and 320 K). E_i represents the assumed error associated to the data of compound i. It is primarily related to the observational uncertainty, but also to the expected ability of the model to reproduce these data. The measurement uncertainty on the $\log_{10}\ p^{0,exp}_{L,i}(T)$ is generally of the order of 0.3. Since the less volatile multifunctional compounds are expected to contribute most to organic aerosol formation, the errors E_i are adjusted in

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order to favour the ability of the method to reproduce their vapour pressures: E_{mono}=0.5 for the monofunctional compounds and E_{multi}=0.3 for the multifunctional compounds. Using these values, we obtain after minimization, $J(298)/N$=0.43 and $J(320)/N$=0.45 for both categories, i.e., the modeled vapour pressures fall well within the range of uncertainty adopted for the observations.

The vapour pressures predictions can be approximated by assuming a linear dependence of $\tau_k(T)$ with T, deduced from their values at 298 and 320 K. Comparisons between predictions and experimental data have been conducted at 290 and 310 K. They show that the prediction uncertainty at 310 K is close to the average of their values at 298 K and 320 K. Predictions at 290 K are found to be of similar uncertainty as those at 298 K. Meaningful comparisons at lower temperatures are difficult due to the lack of experimental data for multifunctional compounds at low temperatures.

The measured vapour pressures are compared with the predictions using this method and using UNIFAC (Asher et al., 2002) in Figs. 3 and 4, respectively. Table 1 shows the standard prediction error for both methods and for each compound class calculated as in UNIFAC as

$$\sigma_i(T) = \frac{\sum_i^n |\log_{10}\ p_{L,i}^{0,\mathrm{exp}}(T) - \log_{10}\ p_{L,i}^{0,\mathrm{mod}}(T)|}{n}, \quad (6)$$

where n is the number of compounds in class i. The poor performance of UNIFAC for dicarbonyls is due to its large error (σ~0.8) for pinonaldehyde, pentanedione and butanedione. Our method performs as well as UNIFAC for monoalcohols. The better performance of our method for diols gives support to the parameterization used to distinguish between isomers. The values of the averaged standard error for alcohols (including monoalcohols and diols) are 0.22 and 0.37 for our method and for UNIFAC, respectively.

The validity of a group contribution method depends on the number and diversity of data it is based on. A drawback of the vapour pressure data set used here is the scarceness of information for heterofunctional species (compounds bearing different

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oxygenated functionalities): vapour pressure data are known for only 4 hydroxy ketones and 2 tri-O-acids species. Both our method and UNIFAC provide fairly good predictions for hydroxy ketones, with $\sigma \lesssim 0.5$ (Table 1). However, they both fail to predict the vapour pressures of tri-O-acids. For example, our $p^0_{L,i}$ prediction for pyruvic acid ($CH_3COCOOH$) is excellent at both temperatures, but a bias of one order of magnitude is obtained in the case of levulinic acid ($CH_3CO(CH_2)_2COOH$) at 320 K. A good agreement with the experimental data is obtained with our method for 2-hydroxy propanoic acid at 298 K. Tobias et al. (2000) deduced the subcooled vapour pressure of α-hydroxytridecyl hydroperoxide on the basis of temperature-programmed thermal desorption (TPTD) analysis ($3\times10^{-9\pm1}$ torr). The value predicted by our method for this hydroxy hydroperoxide is two orders of magnitude higher (see Fig. 3). This difference being much larger than the standard prediction errors calculated for the compounds containing hydroperoxide and/or hydroxy functionality(ies) (monohydroperoxides, monoalcohols, diols, hydroxy ketones, hydroxy acids), this compound was omitted from the dataset used for the minimization. The low measured vapour pressure is surprising since, as noted previously, the closeness of functionalities tends to increase the vapour pressure. Experimental artefacts are not excluded. Further studies are required to better quantify the interactions between functionalities, as well as the role of molecular structure (e.g. presence of substitutions, of cycles) in multifunctional compounds in order to provide satisfactory predictions for the products originating from the oxidation of biogenic hydrocarbons.

Figure 3 shows that our calculated $\log_{10}\ p^0_{L,i}$ for monoalcohols are underpredicted by σ=0.3, while the predictions for the monocarboxylic acids are roughly overpredicted by σ=0.2. These systematic biases for monofunctional classes are related to the oversimplified functional form adopted for parameterizing the vapour pressures. These biases are of little consequence in the context of secondary organic aerosol modeling, however, since the least volatile multifunctional compounds are expected to contribute most to the aerosol mass.

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5. Vapor pressure estimations for α-pinene oxidation products

Figure 5 shows the variation with temperature of the vapour pressure of several important α-pinene degradation products (see MCM 3, Saunders et al., 2003, for identification of the compound), as estimated using the method developed in this work. It is also compared with vapour pressures estimates derived from previous studies, when available.

Bilde and Pandis (2001) measured the melting point and the evaporation rate of solid pinic acid and deduced its vapour pressure over the range 290–323 K. The fusion entropy change ($\Delta S_{fus}(T_m)$) necessary to deduce the corresponding subcooled vapour pressure is unknown for pinic acid. However, NIST (2004) reported the values for $\Delta S_{fus}(T_m)$ for azelaic acid (86 J mol^{-1} K^{-1}) and nonanoic acid (69 J mol^{-1} K^{-1}). Given the presence of two carboxylic functionalities and the non-linear carbon structure of pinic acid, we can assume that $\Delta S_{fus}(T_m)$ of pinic acid lies between these two values. Introducing their average in Eq. (3), we obtain an estimation of the dependence of the subcooled vapour pressure with temperature for this compound (solid line in Fig. 5). Both our method and UNIFAC calculate values which are about a factor of 3 higher than this estimation over the range of ambient temperatures. The agreement is fair given the uncertainty of 50% on the measurements performed by Bilde and Pandis (2001). Jenkin et al. (2004) and Yu et al. (1999) estimated the vapour pressure of the α-pinene oxidation products based on a modified form of the Clausius-Clapeyron equation (Scharzenbach et al., 1993). This equation is function of the boiling point and the molar heat (or entropy) of vaporization. The vapour pressure calculated by Jenkin et al. for pinic acid at 298 K using this equation is about two orders of magnitude higher than the experimentally deduced value at that temperature. This discrepancy could originate from the group contribution method of Joback and Reid (1987) used to estimate the boiling point of pinic acid. This method appears unappropriate for predicting thermodynamical properties of carboxylic diacids. For example, Jenkin et al. (2004) estimate the melting point of pinic acid to be 542 K using this method, 200 K

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above the experimental value (Bilde and Pandis, 2001).

It is important to note that carboxylic acids are known to form dimers in the gas phase (Singleton et al., 1987; Orlando and Tyndall, 2003). For example, at ambient temperature, the vapour pressure of the dimer represents about 90% of the total vapour pressure of acetic acid in equilibrium with its pure liquid phase. Recently, Kuckelmann et al. (2000) observed pinic acid dimers as well as adducts of pinonic acid and pinic acid. The dimers of pinic acid were observed to be abundant. The stability of these dicarboxylic acid dimers can be expected to be high, due to the strong hydrogen bonds formed between the acid groups of the monomers. As in the case of acetic acid, we can expect the partial vapour pressure of the dimer form to contribute significantly to the total vapour pressure for many (di)carboxylic acids, and in particular for pinic acid. It follows that the vapour pressure of the dimer should be close to the experimental total (dimer+monomer) vapour pressure for these compounds. In the pinic acid/pinonic acid adduct, the carbonyl site in one acid group in pinic acid is not H-bonded and therefore able to form an hydrogen bond with another component. Therefore, the vapour pressure of the pinic-pinonic acid adduct should then be on the same order, or even lower, than the vapour pressure of the pinic acid dimer ($\sim 1 \times 10^{-6}$ torr) at ambient temperature.

The vapour pressure estimated by our method for pinonaldehyde agrees well with the measurement of Hallquist et al. (1997). Bilde and Pandis (2001) measured the vapour pressure of pinonic acid to be $\sim 5.3 \times 10^{-7}$ torr at 296 K, but they did not consider this value as reliable, due to experimental problems. UNIFAC predicts vapour pressure values which are an order of magnitude higher than our estimations for these two compounds.

Bonn et al. (2004) is, to our knowledge, the only previous study providing vapour pressure estimations for hydroperoxides, organic nitrates and PANs generated by the oxidation of α-pinene. They provided temperature dependent estimations for the vapour pressure of APINANO3 (Fig. 5). Their estimation uses the group contribution relationship established by Nielsen et al. (1998) which relates the vapour pressure of organic nitrates to their number of carbons and their number of carbonyl, nitrate and

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hydroxy functionalities. The optimization of the contributions is based on a data set including hydrocarbons, alcohols, diols, carbonyls, alkyl nitrates, small hydroxy nitrates and dinitrates of different structures. The influence of the carbon structure on vapour pressure is not taken into account. For C_{10} hydroxy nitrates, this method calculates a vapour pressure of 2×10^{-4} torr at ambient temperature. The vapour pressures we calculate for such compounds, assuming a moderately substituted carbon structure, are $\sim5\times10^{-5}$ torr (primary functionalities), $\sim5\times10^{-4}$ torr (secondary functionalities) and $\sim7\times10^{-3}$ torr (tertiary functionalities). The value of Nielsen et al. (1998) falls therefore well in our range. Our higher values calculated for APINANO3 (Fig. 5) result from the tertiary degree of its nitrate functionality and its branched carbon structure. The vapour pressure relationship proposed by Bonn et al. (2004) for α-pinonyl peroxy nitrate (αP-PAN), a product from the oxidation of pinonaldehyde by OH, is also partly based on the parameterization of Nielsen et al. (1998) for nitrate compounds.

As for the nitrates, our vapour pressure estimates for the hydroperoxides APINAOOH and C96OOH are higher than in Bonn et al. (2004). Bonn et al. (2004) based their estimations on UNIFAC and on vapour pressure data for small hydroperoxides and for the C_{13} hydroxy hydroperoxide measured by Tobias et al. (2000). The exceptionally low vapour pressure of the latter compound has not been taken into account in our derivation of the hydroperoxide contribution, which might explain the discrepancy between our method and Bonn et al. (2004) estimations. As in Bonn et al. (2004), however, we predict a lower vapour pressure for APINAOOH than for C96OOH, due to its hydroxy functionality and its higher carbon number. Taking into account the Tobias et al. (2000) data in the minimization would increase the magnitude of the hydroperoxide contribution (τ_{OOH}), with −3.5231 at 298 K (instead of −2.9942, cfr Table 2). The impact on τ_{OHs} is negligible due to the large amount of data used to constrain this functionality. The vapour pressures of APINAOOH predicted using this alternative value of τ_{OOH} coincide with those determined by Bonn et al. (2004). However, the standard error σ for the hydroperoxide class becomes very large, increasing from 0.2 (Table 1) to 1.3.

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6. Conclusions

A group contribution method has been proposed to predict the vapour pressure of the products generated by the oxidation of α-pinene. Parameterizations are derived for the influence of the carbonyl, hydroxy, nitrate, peroxy acyl nitrate, acid and hydroperoxide functionalities. The impact of alkyl substitutions is also parameterized for alcohols and nitrates. The predicted vapour pressures are within a factor 2–3 of the experimental values for multifunctional compounds. Further experimental studies are required to investigate 1) the effect of the substitutions, 2) the effect of the distance between functionalities on the vapour pressure and 3) the vapour pressure of heterofunctional compounds.

Our findings support the hypothesis that, among the α-pinene products identified to date, dicarboxylic acids and hydroxy acids such as pinic acid and hydroxy pinonic acid are the least volatile compounds, with estimated vapour pressures of 3×10^{-6} and 6×10^{-7} torr, respectively. Other primary products can be considered as semi-volatile, with p_L^0 ranging between 1×10^{-5} and 1×10^{-3} torr. Among them, hydroxy hydroperoxides present the lowest vapour pressures. Compounds produced after several oxidation steps in the α-pinene mechanism may have low volatilities due to their increased number of functionalities. However, they are expected to contribute less significantly to the aerosol phase because of their lower yields. Hydroperoxides are expected to contribute more largely to SOA formation at low temperatures due to the strong dependence of the hydroperoxide group contribution with temperature. In any case, the contribution of these semi-volatile products to the aerosol phase is expected to be less important than predicted by Bonn et al. (2004). The dimerization of multifunctional carboxylic acids is believed to take place in laboratory experiments of α-pinene oxidation. Since dimers are expected to contribute largely to the total (dimer+monomer) concentration of multifunctional carboxylic acids in these conditions, their partial vapour pressure is likely to be close to the vapour pressure measured in the laboratory for these compounds. The pinic/pinonic acid adduct is likely to play a significant role in

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the observed partitioning of pinonic acid (Yu et al., 1999) between the aerosol and gas phases, due to its low vapour pressure estimated in this study ($\leq 1\times10^{-6}$ torr). However, the role of dimers and adducts remains difficult to quantify in absence of kinetic data for their stabilities and formation rates.

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Table 1. Literature data used in this work, and standard error (as defined by Eq. 6) between the experimental and estimated vapour pressures, using the method developed in this work and using UNIFAC.

Class of compounds	$\sigma(298\,K)$ This work	$\sigma(298\,K)$ UNIFAC	$\sigma(320\,K)$ This work	$\sigma(320\,K)$ UNIFAC	Sources
Monocarbonyls	0.21	0.36	0.16	0.29	Lide (2001), ESDU (2001)
Dicarbonyls	0.26	0.56	0.15	0.65	HSDB (2004), Lide (2001), Hallquist et al. (1997)
Prim.[d] mononitrates	0.33	–[b]	0.22	–[b]	Lide (2001)
Prim.[d] *n*-monoalcohols	0.34	0.21	0.34	0.18	Poling et al. (2001)
Sec.[d] monoalcohols	0.29	0.29	0.29	0.24	Poling et al. (2001)
Tert.[d] monoalcohols	0.12	0.27	0.06	0.27	Poling et al. (2001)
PAN-like compounds	–[a]	–[b]	–[a]	–[b]	Bruckmann and Willner (1983)
Monohydroperoxides	0.21	–[b]	–[a]	–[b]	Lide (2001), HSDB (2004)
(prim.)[d] *1,n*-dinitrates	0.11	–[b]	–[c]	–[b]	Fischer and Ballschmiter (1998)
1,2-dinitrates	0.35	–[b]	–[c]	–[b]	Fischer and Ballschmiter (1998)
Sec.[d] dinitrates	0.11	–[b]	–[c]	–[b]	Fischer and Ballschmiter (1998)
(prim.)[d] *1,n*-diols	0.21	0.40	0.23	0.31	ESDU (2001)
Sec.[d] diols	0.20	0.26	0.15	0.22	ESDU (2001)
Tert.[d] diols	0.14	0.89	0.13	0.78	ESDU (2001)
Other[e] diols	0.28	0.38	0.29	0.43	ESDU (2001)
n-carboxylic acid	0.27	0.11	0.04	0.11	Poling et al. (2001)
1,n-dicarboxylic acid	0.26	0.65	0.45	0.48	Bilde et al. (2003)
Hydroxy ketones	0.43	0.58	0.34	0.50	Lide (2001), Asher et al. (2002)
Tri-O-acids[f]	0.42	0.50	0.61	0.60	HSDB (2004), ESDU (2001)

[a] Only one experimental value. [b] Not parameterized. [c] No experimental data. [d] Refers to the degree of substitution of the carbon(s) to which the functionality(ies) is(are) attached. Read "prim." as "primary", "sec." as "secondary", and "tert." as "tertiary". [e] The carbons bearing the functionalities have different degrees of substitutions. [f] Acid compounds with a carbonyl or hydroxy functionality.

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Table 2. Optimized group contributions (τ_k), as functions of the temperature (T). The last column reports the number of species for which experimental data are available in each class.

Class of compounds	Abr.	Contribution	Nb. of Species
Carbonyls	τ_{carb}	−0.8937+0.0039*(T-298)	16
Primary[a] nitrates	τ_{ONO2p}	−2.0897+0.0063*(T-298)	16
Secondary[a] nitrates	τ_{ONO2s}	−1.6711+0.0063*(T-298)	14
Tertiary[a] nitrates	τ_{ONO2t}	−1.2793+0.0063*(T-298)	0
Hydroperoxides	τ_{OOH}	−2.9942+0.0361*(T-298)	3
Primary[a] alcohols	τ_{OHp}	−2.6738+0.0171*(T-298)	28
Secondary[a] alcohols	τ_{OHs}	−2.0374+0.0124*(T-298)	22
Tertiary[a] alcohols	τ_{OHt}	−1.4418+0.0103*(T-298)	7
Acids	τ_{COOH}	−3.2516+0.0075*(T-298)	13
PANs	τ_{PAN}	−3.0372+0.0133*(T-298)	1

[a] Refers to the degree of substitution of the carbon(s) to which the functionality(ies) is (are) attached.

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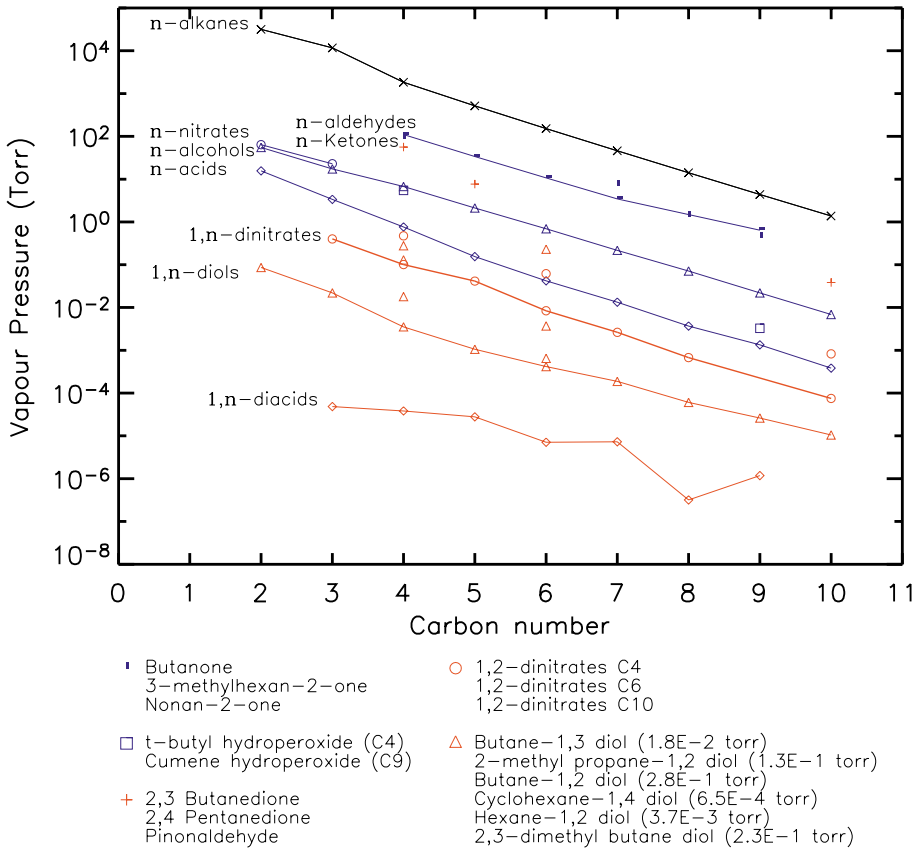

Fig. 1. Vapor pressures of monofunctional and difunctional compounds at 298 K. Species prefixed by "*n-*" or "*1,n-*" (connected symbols) are of type "$CH_3-(CH_2)_n-X$" or "$X-(CH2)_n-X$", respectively, with X being an oxygenated functionality. Non-connected symbols are used for all other types of compounds.

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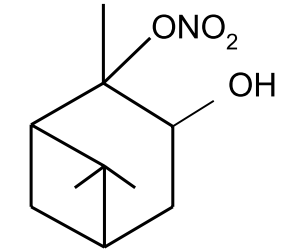
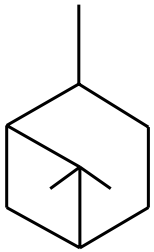
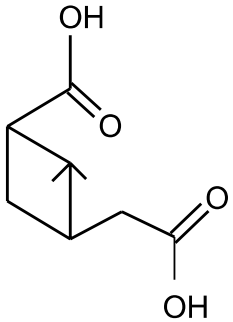


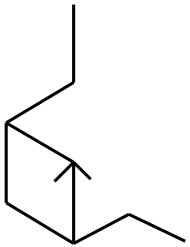
APINANO3



APINANO3 parent compound



Pinic acid



Pinic acid parent compound

Fig. 2. Structure of APINANO3 and pinic acid with their respective alkanoic parent compound.

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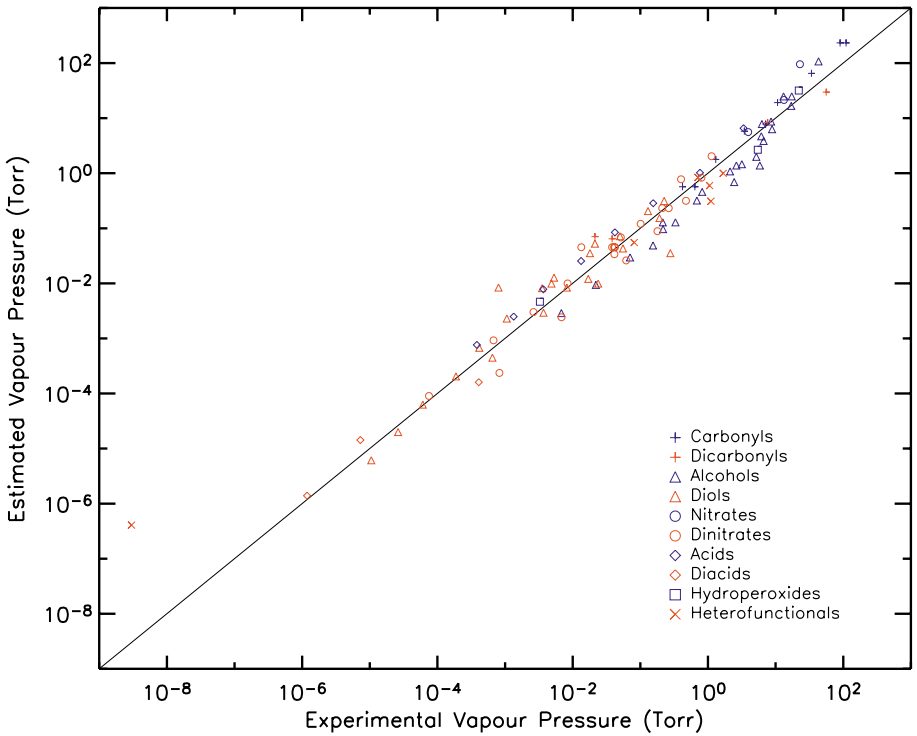

Fig. 3. Vapor pressures estimated using the prediction method developed in this work against the experimental vapour pressures (sources in Table 1). Monofunctional and difunctional compounds are represented in blue and red, respectively.

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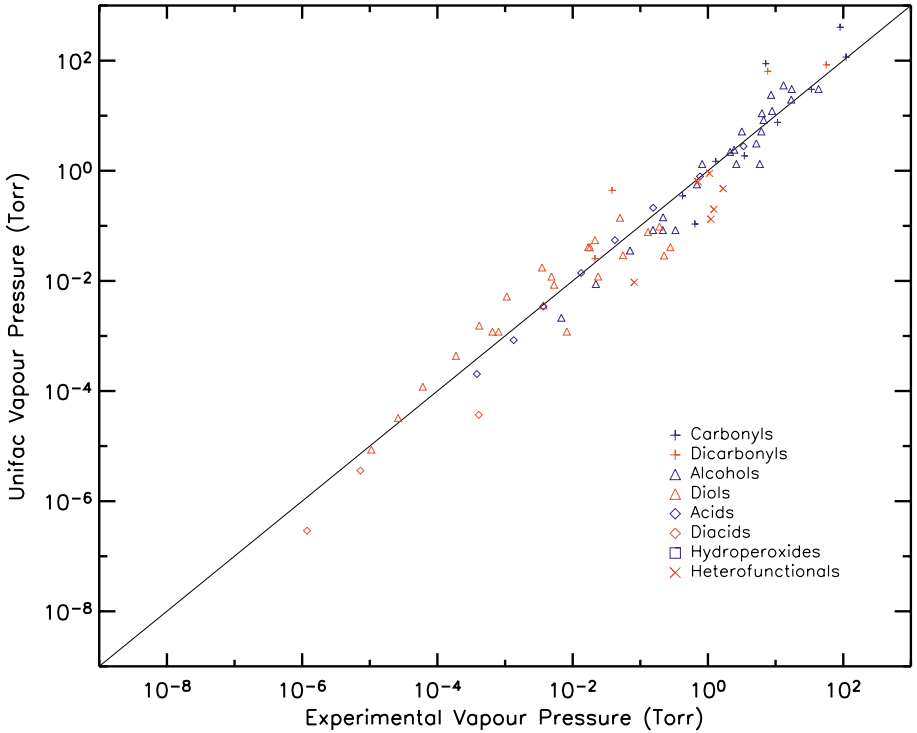

Fig. 4. Vapor pressures estimated using UNIFAC against the experimental vapour pressures (sources in Table 1). Monofunctional and difunctional compounds are represented in blue and red, respectively.

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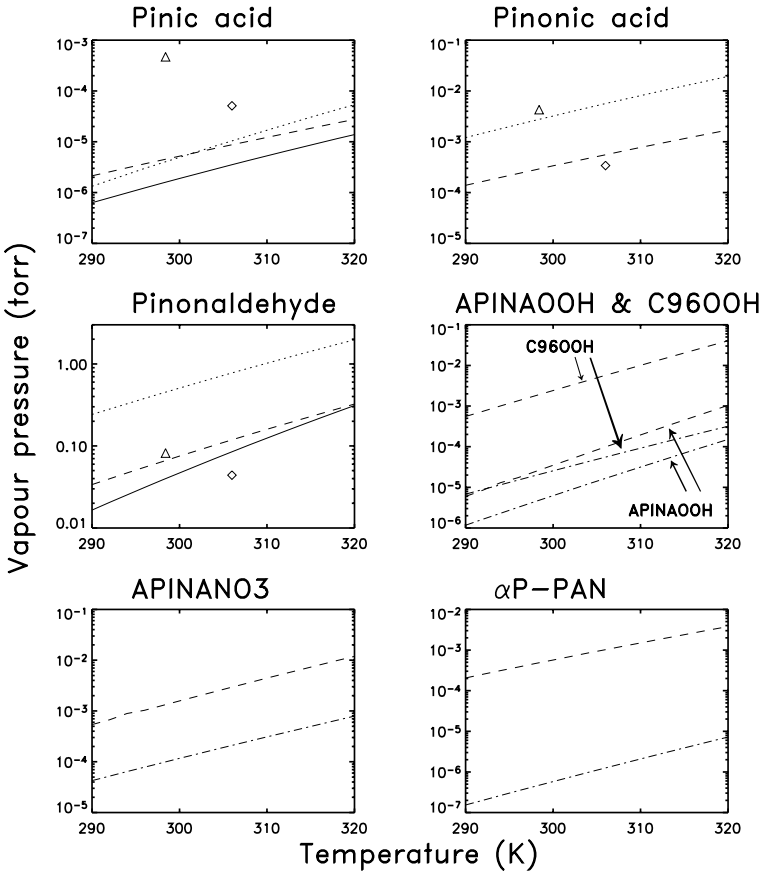

Fig. 5. Vapor pressure of individual compounds estimated from the measurements (solid line), the method developed in this work (dashed), the UNIFAC method Asher et al. (2002) (dotted), Bonn et al. (2004) (dash dotted), Jenkin et al. (2004) at 298 K (triangles) and Yu et al. (1999) at 306 K (diamonds).

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